

# Spatial variability of atrazine dissipation in an allophanic soil

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**Abstract:** The small-scale variability (0.5 m) of atrazine (6-chloro-*N*<sup>2</sup>-ethyl-*N*<sup>4</sup>-isopropyl-1,3,5-triazine-2,4-diamine) concentrations and soil water contents in a volcanic silt loam soil (Haplic Andosol, FAO system) was studied in an area of 0.1 ha. Descriptive and spatial statistics were used to analyse the data. On average we recovered 102% of the applied atrazine 2 h after the herbicide application (CV = 35%). An increase in the CV of the concentrations with depth could be ascribed to a combination of extrinsic and intrinsic factors. Both variables, atrazine concentrations and soil water content, showed a high horizontal variability. The semivariograms of the atrazine concentrations exhibited the pure nugget effect, no pattern could be determined along the 15.5-m long transects on any of the seven sampling days over a 55-day period. Soil water content had a weak spatial autocorrelation with a range of 6–10 m. The dissipation of atrazine analysed using a high vertical sampling resolution of 0.02 m to 0.2 m showed that 70% of the applied atrazine persisted in the upper 0.02-m layer of the soil for 12 days. After 55 days and 410 mm of rainfall the centre of the pesticide mass was still at a soil depth of 0.021 m. The special characteristics of the soil (high organic carbon content, allophanic clay) had a strong influence on atrazine sorption and mobility. The mass recovery after 55 days was low. The laboratory degradation rate for atrazine, determined in a complementary incubation study and corrected for the actual field temperature using the Arrhenius equation, only accounted for about 35% of the losses that occurred in the field. Results suggest field degradation rates to be more changeable in time and much faster than under controlled conditions. Preferential flow is discussed as a component of the field transport process.

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**Keywords:** atrazine; spatial variability; persistence; leaching; preferential flow

## 1 INTRODUCTION

The major processes involved in dissipation of pesticides applied to the soil surface are volatilisation, degradation (including microbiological and hydrolytic breakdown), plant uptake, leaching to groundwater and runoff to surface waters. Interactions between the pesticide and the soil, such as sorption processes, influence the chemical's fate in soil. Soil organic carbon content ( $C_{org}$ ) is widely used to estimate sorption for pesticide transport.<sup>1</sup> For polar chemicals, such as atrazine, clay content and composition as well as the soil pH also affect sorption.<sup>2</sup> Microbiological transformation is the most relevant process for the degradation of atrazine in the soil environment.<sup>3,4</sup> Its efficacy is mainly dependent on soil temperature, soil water content and soil pH.<sup>5,6</sup> Thus atrazine leaching mainly depends on soil water content, texture, pH and organic carbon content of the soil as

well as soil hydraulic properties.<sup>7,8</sup> In recent years the rapid movement of pesticides along preferential pathways such as cracks and root channels has been considered as an important pathway for groundwater contamination.<sup>7,9,10</sup> Through preferential flow, pesticides move quickly to the subsoil irrespective of their chemical properties.<sup>11</sup> The exact conditions under which preferential flow occurs in the field are not yet fully understood,<sup>12</sup> but there is likely to be an interaction between initial soil water content and preferential flow.

Significant variability of soil physical and chemical properties has been reported in the past.<sup>13</sup> Several studies have shown, for example, that water content of the upper soil layer is highly variable.<sup>14</sup> Generally, the heterogeneity of soil properties is site-specific. It can be very short ranged, long ranged or purely stochastic. Thus, it has to be determined for each site. Our

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hypothesis was that heterogeneities in physical and chemical soil properties would have an impact on pesticide transport mechanisms, degradation and sorption and would create non-uniform areas of pesticide concentrations on the field scale (intrinsic factors).<sup>15</sup> Observed variations in pesticide concentrations can also result from a lack of uniformity in pesticide application (the extrinsic factor).

Conventional field experiments used to assess the risk of pesticide leaching are often based on widely spaced sampling sites (eg up to 10 m apart).<sup>16,17</sup> The sampling, normally done using vertical increments of 0.3 m or more,<sup>18</sup> can be too coarse to track pesticides in the upper few centimetres of the soil soon after surface application. Much interesting information about spatial variability of soil processes is also lost by bulking of soil samples.<sup>19</sup> Spatial variability of pesticide sorption has been analysed on larger scales (>1 ha).<sup>8,20–24</sup> Small scale variability of pesticide persistence has rarely been analysed in field trials.<sup>25,26</sup> Studies concentrating on the persistence of pesticides close to the soil surface are even fewer in number.<sup>27</sup>

The aims of this investigation were to determine atrazine dissipation and movement near the soil surface (0–0.2 m depth) and to study the small-scale (0.5 m) spatial variability of soil water content and atrazine concentration. For this purpose a field experiment was carried out with atrazine application and subsequent sampling at the 0.5 m scale on a 0.1 ha area. As it can be difficult to distinguish the contributions of degradation and transport processes to pesticide dissipation in a field trial, a complementary degradation trial was conducted under controlled conditions in the laboratory. Atrazine was chosen for this study because it is widely used in New Zealand's cropping system, where pastures regularly succeed crops and herbicide residues from the preceding crops can pose risks for *Lolium perenne* L and *Trifolium spec*, the two main components of the pasture.

## 2 MATERIALS AND METHODS

### 2.1 Research area

The study was conducted on the Waikato Research Orchard located near Hamilton, New Zealand. The

soil is volcanic (Bruntwood silt loam), which is a Haplic Andosol according to the FAO classification. The main soil characteristics were determined by samples adjacent to the experimental area and are presented in Table 1. Soil particle size distribution was determined by the hydrometer method of Day,<sup>28</sup> the bulk density with undisturbed soil cores, soil particle density by a pycnometer, the porosity using the data of particle and bulk density and the organic carbon content according to the method of Merry and Spouncer.<sup>29</sup>

The clay content is moderate and somewhat variable through the profile (range 15–25%), whereas the organic carbon content is high in the soil surface (8.7%) and decreases significantly with depth. The bulk density is fairly low throughout the profile (average of 0.77 g cm<sup>-3</sup>) due to the high content of allophanic clays.

The site was previously under maize (*Zea mays* L) that was harvested in April 2000. Harrow tillage was performed following harvest, aimed at levelling the site. Precipitation and temperature were monitored using data from a weather station located within 1 km of the site.

### 2.2 Pesticide application

Prior to the application of atrazine, soil samples were taken at the four corners of the experimental area to determine background levels of atrazine in the upper 0.2 m of the soil. After 10 mm rain the fallow soil was regarded as settled and soil samples were taken to establish the initial soil water content. Atrazine 500 g litre<sup>-1</sup> SC (Gesaprim 500 FW<sup>®</sup>; Novartis, Basel) was applied on 03 May 2000 at a rate of 3 kg AI ha<sup>-1</sup> in 300 litre ha<sup>-1</sup> water, using a hand-held carbon-dioxide-pressured precision sprayer equipment with TeeJet 11004TTVP nozzles operated at 230 kPa, a walking speed of 1 m s<sup>-1</sup> and a boom width of 0.75 m.

### 2.3 Soil sampling

The downward migration of the atrazine pulse into the soil was monitored using vertical soil samples collected with a soil borer. The soil corer contained a 0.05 m ID × 0.3 m long tube. This soil sampling

**Table 1.** Soil properties of the Bruntwood silt loam, Hamilton

		Sand	Silt	Clay		$\varphi^b$	$\rho^c$	
Horizon	Depth (m)	(%)			OC <sup>a</sup> (%)	(g cm <sup>-3</sup> ) (±SD) <sup>d</sup>		Porosity (%) (±SD) <sup>d</sup>
Ap	0.00–0.05	39	36	25	8.7	2.32 (±0.02)	0.75 (±0.02)	68 (±1.25)
ApBw	0.05–0.20	35	40	25	5.9	2.36 (±0.02)	0.77 (±0.01)	67 (±0.49)
Bw	0.20–0.45	40	45	15	1.9	2.42 (±0.01)	0.77 (±0.02)	68 (±0.83)
Bg	0.45–0.64	48	27	25	0.3	2.47 (±0.02)	0.74 (±0.04)	70 (±1.30)
Brg1	0.64–0.76	34	41	25	0.2	2.43 (±0.03)	0.77 (±0.01)	68 (±0.61)
Brg2	0.76–0.95	34	45	21	0.2	2.45 (±0.04)	0.81 (±0.09)	67 (±3.86)

<sup>a</sup> OC, soil organic carbon content.

<sup>b</sup>  $\phi$ , soil particle density.

<sup>c</sup>  $\rho$ , soil bulk density.

<sup>d</sup>  $n = 3$ .

technique was chosen because ceramic solution samplers have proven inadequate for sampling the total soil concentration of pesticides.<sup>30</sup>

Forty-one soil samples were collected 2 h after the application so as to check atrazine coverage: 31 samples 0.5 m apart along a transect and further 10 samples 0.5 m apart along a second perpendicular transect. Sampling took place on six other occasions after each significant amount of rainfall (>20 mm). Transects parallel to the initial transect were sequentially sampled using 30 cores 0.5 m apart along the 15.5 m long transects.

The soil cores were stored at  $-18^{\circ}\text{C}$  until analysis. They were cut into 0.02-m thick slices, each representing one sampling depth. The first millimetre of the circumference of each slice was discarded in order to prevent cross-contamination between the different sampling depths. Each core slice was thoroughly homogenised before sub-sampling for determination of atrazine and water content.

## 2.4 Laboratory materials and methods

### 2.4.1 Degradation study

Soil from the surface layer (0–0.1 m) of the field trial site was collected and used for a degradation experiment under controlled environmental conditions in the laboratory. Aliquots of the soil (50 g dry weight) in 250-ml volumetric flasks were adjusted to 60% of the maximum water-holding capacity of the soil. Each soil sample was fortified with an aqueous dispersion (1 ml) of the formulated product, equivalent to the application rate of  $3 \text{ kg AI ha}^{-1}$  used in the field trial. The flasks were incubated at 10, 20 and  $30^{\circ}\text{C}$ . The soil water content was adjusted to the pre-determined weight twice a week. Two flasks were taken from each temperature after 0, 3, 7, 14, 21, 28, 42 and 56 days and stored at  $-18^{\circ}\text{C}$  until analysis.

### 2.4.2 Field water content

The gravimetric soil water content was determined for each soil slice using a random sub-sample of approximately 5 g of soil. The samples were dried at  $105^{\circ}\text{C}$  until no reduction in weight could be recorded. The volumetric water content was calculated using the average bulk density of the soil (Table 1).

### 2.4.3 Extraction of atrazine

Soil samples (5–50 g, depending on weight of soil available) were placed in volumetric flasks and mixed with methanol + purified water (70 + 30 by volume) at a ratio of 1 g of air-dried soil to 2 ml of solvent, and spiked with  $20 \mu\text{g}$  terbuthylazine ( $N^2$ -*tert*-butyl-6-chloro- $N^4$ -ethyl-1,3,5-triazine-2,4-diamine) as an internal standard. The flasks were then shaken on an orbital shaker for 1 h at  $230 \text{ rev min}^{-1}$  and  $20^{\circ}\text{C}$ . The suspensions were allowed to settle for at least 30 min and an aliquot of the supernatant solution was then diluted 1 + 10 by volume with deionised water. Solid phase extraction was used to clean up and concentrate the samples. The samples were aspirated through

$\text{C}_{18}$  columns (Alltech, Deerfield, 2.8 ml, 0.5 g  $\text{C}_{18}$  sorbent material). The adsorbed atrazine was eluted with methanol (2 ml), the eluent collected, evaporated under a gentle stream of nitrogen and the residue dissolved in methanol + purified water (50 + 50 by volume; 1 ml) for analysis by high performance liquid chromatography (HPLC).

### 2.4.4 Analysis

HPLC analysis was performed on a Shimadzu LC-6B system with a Luna  $\text{C}_{18}$  (4.6 mm ID  $\times$  15 cm) column. The mobile phase was methanol + water (60 + 40 by volume) at a flow rate of  $1 \text{ ml min}^{-1}$ . The injection volume was  $50 \mu\text{l}$ . The resulting retention times for atrazine and terbuthylazine were 8.4 min and 5.3 min, respectively. Detection was performed by UV absorption at 220 nm. The identity of atrazine was confirmed at regular intervals by making additional peak measurements at wavelengths of 260 and 280 nm.

The samples for atrazine recoveries were prepared by adding known amounts of atrazine to 25 g of uncontaminated soil (10 repetitions), at  $8000 \mu\text{g kg}^{-1}$ , which is about three times lower than the field application rate. The average recovery efficiency was 91% with a coefficient of variation (CV) of 3.6%.

## 2.5 Statistical analysis

### 2.5.1 Descriptive statistics

The distribution of the two variables, atrazine concentration and soil water content, was analysed statistically with the assumption that, for a given depth, the variables were statistically independent regardless of their spatial position. Statistical characteristics of the data set used in this study were the median, the standard deviation and the coefficient of variation. Furthermore, the Shapiro–Wilk test was used to determine how nearly normal the data were distributed. Spearman rank correlation coefficients between soil water content and atrazine concentrations were calculated.<sup>31</sup>

### 2.5.2 Spatial statistics

A geostatistical analysis was carried out to investigate the spatial correlation structure or the distance over which both variables, the atrazine concentration and the soil water content, were correlated. The dissimilarity between the observations as a function of their separation distance  $h$  can be described using semivariograms. The average dissimilarity is measured by the experimental semivariogram, which is calculated as half of the average difference between the components of every data pair separated by the vector  $h$ :

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [x(i) - x(i+h)]^2 \quad (1)$$

where  $N(h)$  is the number of data pairs available for a given distance  $h$ ,  $x(i)$  is the value of the first of the

pair and  $x(i+h)$  is the corresponding end value.<sup>32</sup> Semivariograms were created up to half the maximum lag distance.<sup>33</sup> The structure of spatial dependence of the parameters can be determined by trial fitting different models to the data. Exponential, spherical, Gaussian and linear models with and without a nugget effect were tested. A detailed description of the models and their parameters is given, for example, by Cressie<sup>34</sup> and by Deutsch and Journel.<sup>35</sup> Applying Levenberg–Marquardt's non-linear least-squares procedure<sup>36</sup> the models were fitted to the derived experimental semivariogram. The value of the nugget effect ( $C_0$ ) was estimated by extrapolating experimental semivariogram estimates from the lags closest to zero. To judge which of the models is best, the Akaike's information criterion AIC was used. According to Webster and McBratney<sup>37</sup> it can be calculated from the residual sum of squares  $R$  of deviations from the fitted model with:

$$\text{AIC} = n \ln(R) + 2p \quad (2)$$

where  $n$  is the number of points on the variogram at which the semivariance is estimated and  $p$  is the number of parameters in the model. The model to choose is the one for which the value of AIC is smallest.

### 3 RESULTS AND DISCUSSION

#### 3.1 Degradation under controlled temperature and soil moisture

Degradation of atrazine in the laboratory was well described by first-order kinetics with regression coefficients being greater than 0.9. Temperature had a significant effect on degradation (Table 2). During the 56-day incubation period 40, 92 and 96% of the applied atrazine was degraded at 10, 20, 30 °C, respectively.

#### 3.2 Variability of soil water content and atrazine in the field experiment

The 2D spatial variability of soil water content and atrazine concentrations was studied on each sampling day by analysing the 30 samples taken along one of the transects.

**Table 2.** Degradation half-lives of atrazine in the field and under controlled temperature and 60% maximum-water-holding capacity in the Bruntwood silt loam soil; regressions for the degradation described by first-order kinetics and coefficients of regression ( $R^2$ )

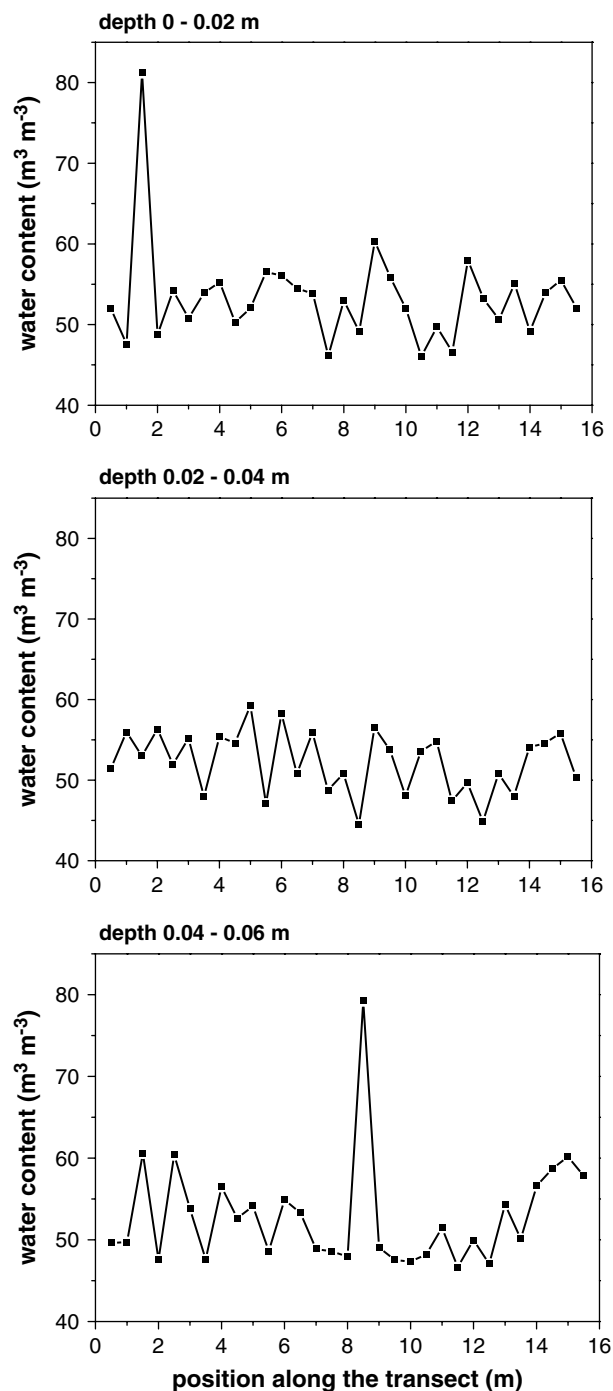
Temperature (°C)	Half-life (days)	Regression ( $x$ , days after application; $y$ , residue in $\mu\text{g kg}^{-1}$ )	$R^2$
10	79	$\log y = -0.0038x + 3.6337$	0.98
20	13	$\log y = -0.0215x + 3.6427$	0.98
30	9	$\log y = -0.0319x + 3.5146$	0.92
7.5 <sup>a</sup>	12	$\log y = -0.025x + 4.3513$	0.85

<sup>a</sup> Average soil temperature (0–10 cm depth) during the field investigation period.

#### 3.2.1 Variability of soil water content

All distributions of the soil water content, ( $\theta$ ), differed significantly from the normal distribution due to the occurrence of outliers, with both very high and low water contents. Soil water content was influenced by soil texture and topographic position (Fig 1).

Some water content profiles are represented in Fig 2. Presence of vertical variability can be seen with  $\theta$  increasing downward, eg on 03 May (CV = 10%), but also with fluctuating water contents, eg on 02 June (CV = 11%). There is also a significant amount of horizontal variability, indicated by the error bars



**Figure 1.** Spatial distribution of the soil water contents for 03 May for the first three sampling depths.

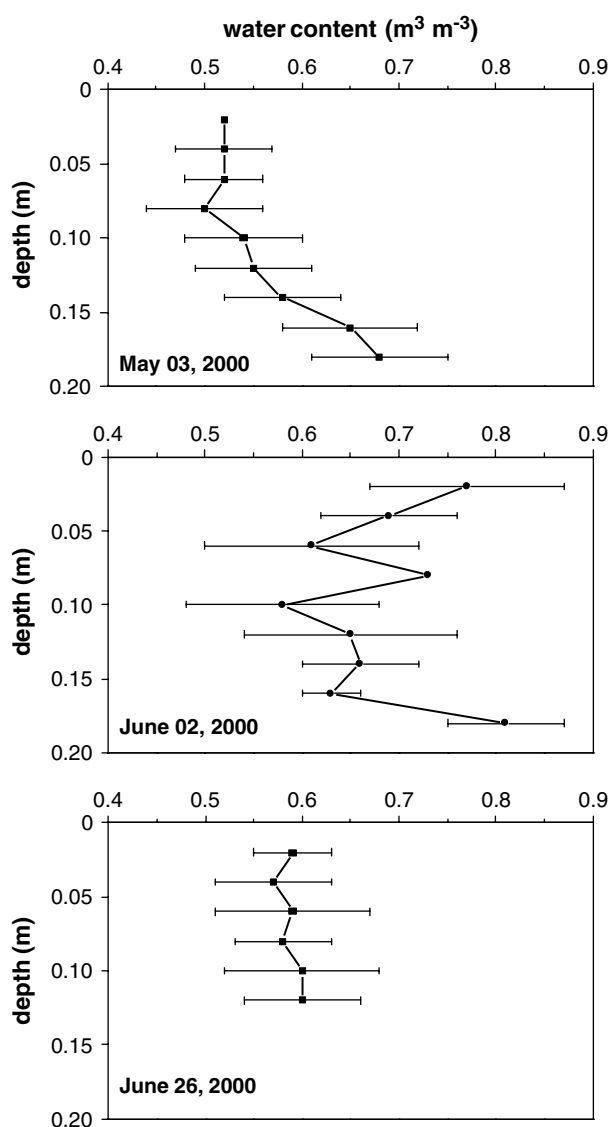


Figure 2. Observed soil water contents (mean  $\pm$  standard deviation).

for the water content in each sampling depth. The coefficients of variation ranged between 9 and 19%. The CV values were for the most part consistently lower at the first depth interval than at deeper depths. Solar radiation and wind on the surface could be a significant influence on the water content in the surface layer, whereas preferential flow may explain the variation in deeper layers.

For the spatial statistics of soil water content, the data collected from the first three layers (0–0.06 m) were taken together to obtain a large enough data set for a semivariogram analysis in the horizontal direction.<sup>38,39</sup> For the first two sampling days (03 May, 09 May) the semivariograms show a pure nugget effect ( $C_0$ ). Nugget effects represent the spatial variability that is not detected at the shortest sampling distance (0.5 m).<sup>40</sup> No valid spatial structure could be inferred with the four models tested. This might be due to the limited sampling size or to the limited spatial resolution. The latter would mean that there is no spatial dependence at the scale of investigation since

all of the variance occurs within the smallest sampling interval (the range of the semivariogram model  $a$  would be smaller than 0.5 m in the horizontal direction). Observing the data presented in Fig 1, a failure due to an underlying trend across a transect can be excluded for all three depths. Netto *et al*<sup>41</sup> found the same lack of spatial structure for soil water content on a brown eluviated soil. The vertical (1.2 m transects) and horizontal (1.05 m depth) sampling resolutions were with 0.1 m even finer than in the study presented here.

Semivariograms for  $\theta$  on later sampling days (15 May, 02 June, 06 June) show weak spatial horizontal dependence with apparently very high nugget effects and with large range values (Fig 3). According to the AIC selection criteria the spherical model is the best fit to the experimental semivariances (AIC = -46.36). Nevertheless, there was considerable uncertainty in the model parameters as expressed by their high standard deviations ( $C_0$  0.6,  $c$  0.7,  $a$  12.4). Models including nugget effect best described the experimental variances. The nugget values accounted for 70% of the total sample variance. Thus, the high nugget values indicate largely random or inherently variable soil water content in the experimental site. The range of a semivariogram provides an estimate of the extent of the spatial dependence. For the samples taken on 15 May, 02 June and 06 June the ranges were within 6–10 m. This distance represents the minimum average distance at which the maximum variation occurred. Sills of the semivariograms were similar to the sample variance. The data gathered on the first two sampling days showed no spatial structure at all, whereas data for later sampling days showed a weak autocorrelation. This may be explained by the structure of the water phase being more incoherent in soils with lower water contents.

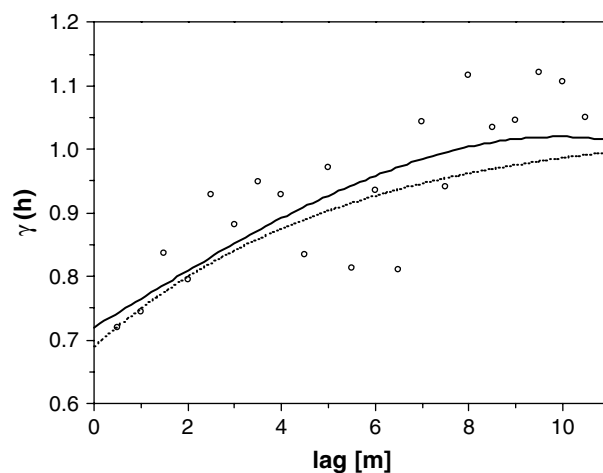


Figure 3. Experimental semivariogram of the normalised soil water contents for 15 May (sampling depth: 0–0.06 m). The dotted line represents the fitted theoretical variogram applying the exponential model ( $\gamma(h) = 0.69 + 0.35(1 - e^{-3h/12.4})$ ), the solid line represents the spherical model ( $0.72 + 0.3(1.5h/9.93 - 0.5(h/9.93)^3)$ ).

### 3.2.2 Variability of the atrazine concentrations

Coefficients of variation (CV) for atrazine concentrations were quite high ( $\leq 100\%$ , Tables 3 and 4). Walker and Brown<sup>24</sup> concluded from their field experiment with simazine that the principal reason for the variability in herbicide residues was the unevenness in the herbicide application. In contrast to their conclusion, the observed increase in the CV of atrazine concentrations with depth demonstrates that the residue variability in our study was a combined result from a non-uniform application (extrinsic factor) and from natural variations in soil characteristics (intrinsic factors).<sup>15</sup> Two hours after the pesticide application we took 41 samples to assess the performance of the application. The expected concentration of atrazine in the top 0.02 m immediately after the application of 3 kg AI ha<sup>-1</sup> can be calculated using the measured bulk density of 0.75 g cm<sup>-3</sup> as 20 000 µg kg<sup>-1</sup> soil. The mean measured atrazine concentration was 20 340 µg kg<sup>-1</sup> soil with a standard deviation of 7200 µg kg<sup>-1</sup> soil and a CV of 35%. Since the variability of the atrazine surface deposition was considerable, the observed horizontal variability in atrazine concentrations in the lower soil profile will be due to both intrinsic and extrinsic factors. Pesticide application variability is inherent. Drift while spraying, volatilisation, etc inhibit an even application. A CV of 35% for pesticide application ( $n = 41$ ) is acceptable and comparable with other studies.<sup>23,25,42–45</sup>

Statistical moments for the atrazine mass are summarized in Tables 3 and 4 for the different layers and sampling days. Inspecting the raw data presented in Fig 4, the distribution of atrazine concentrations reveals no trend across the transects for any of the sampling days. The assumption of non-stationarity of the data for the geostatistical analysis is fulfilled. Analysing the semivariances plotted against distance, the horizontal short distance correlation of atrazine concentrations was non-significant for all sampling days (Fig 5). No autocorrelation is observed, the semivariograms having apparently only the pure nugget effect. The semivariances oscillate around the variance. This means that either the sampling was still too coarse to capture the spatial structure of the atrazine distribution or that the variability was stochastic in nature. With the exception of the samples taken on 15 May, the concentrations declined with depth. Very often the pattern in the third sampling layer (0.04–0.06 m) can be traced back to the upper soil layers. The vertical variability was generally larger than the horizontal variability. All distributions except those of the application day and of 15 May (depth 0.04–0.06 m) differed significantly ( $P < 0.05$ ) from the normal distribution. This, and also the large CV values, might be an indication of some non-uniform herbicide degradation, sorption or transport. Several authors have reported vertical spatial variability in atrazine sorption or degradation

**Table 3.** Soil residues and rainfall data for the 55-day period following atrazine application on 03 May 2000

Sampling date	Atrazine residue (kg ha <sup>−1</sup> ) at sampling depth (m)									Interval rainfall <sup>d</sup> (mm)
	0–0.02			0.02–0.04			0.04–0.06			
	Z <sup>a</sup>	CV <sup>b</sup>	W <sup>c</sup>	Z <sup>a</sup>	CV <sup>b</sup>	W <sup>c</sup>	Z <sup>a</sup>	CV <sup>b</sup>	W <sup>c</sup>	
03.05.00	2.99	35	0.51							
09.05.00	3.93	22	0.92	0.22	62	0.16	0.02	49	0.01	49.3
15.05.00	2.11	36	0.77	0.57	50	0.29	0.02	57	0.02	68.8
02.06.00	0.26	63	0.00	0.1	32	0.09	0.01	63	0.00	111.1
06.06.00	0.16	25	0.00	0.05	35	0.06	0.01	53	0.00	122.9
26.06.00	0.09	23	0.01	0.03	39	0.05	0.01	33	0.16	27.7

<sup>a</sup> Z: Values are the median of 30 soil samples taken 0.5 m along a transect.

<sup>b</sup> CV, coefficient of variation (%).

<sup>c</sup> W, coefficient of the Shapiro–Wilk test.

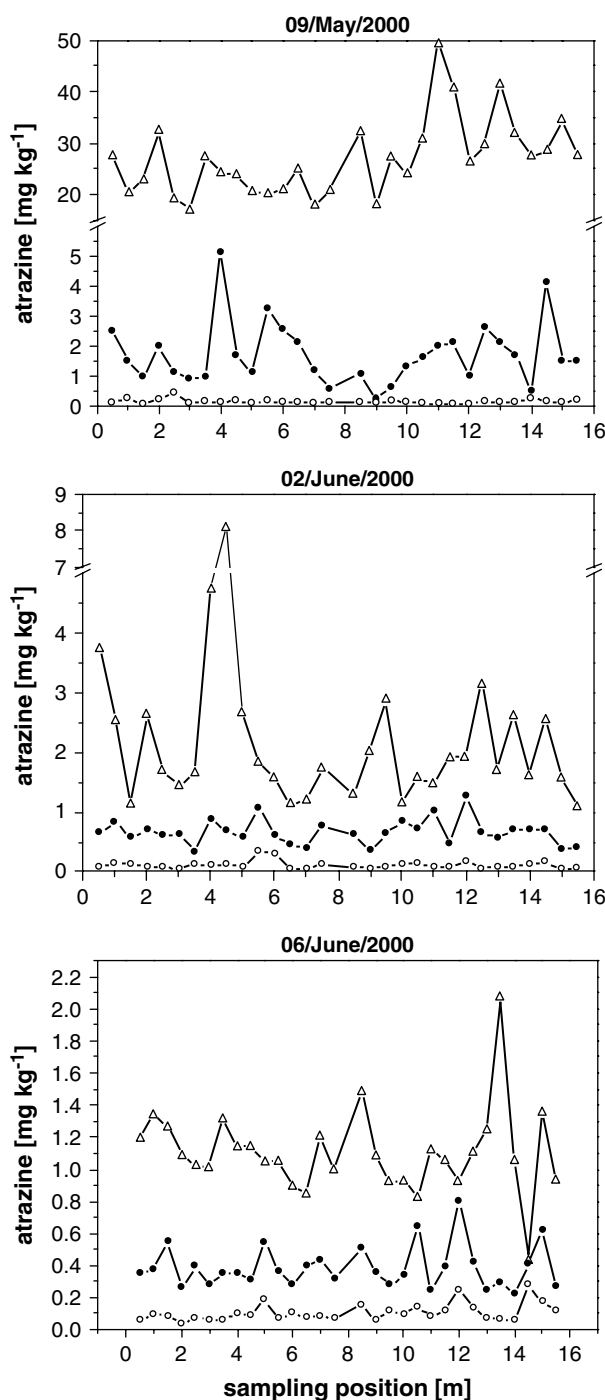
<sup>d</sup> Rainfall is the accumulated precipitation amount for the periods between sampling.

**Table 4.** Residues of atrazine in soil below 0.06 m for the 55-day period following atrazine application on 03 May 2000

Sampling date	Atrazine soil residues (kg ha <sup>-1</sup> ) at sampling depth (m)									
	0.06–0.08		0.08–0.1		0.1–0.12		0.12–0.14		0.14–0.16	
	Z <sup>a</sup>	CV <sup>b</sup>	Z <sup>a</sup>	CV <sup>b</sup>	Z <sup>a</sup>	CV <sup>b</sup>	Z <sup>a</sup>	CV <sup>b</sup>	Z <sup>a</sup>	CV <sup>b</sup>
15.05.00	0.01	85	0.01	45	0.01	39	0.004	75	0.002	100
02.06.00	0.006	80	0.004	39	0.005	49	0.003	99	0.001	151
26.06.00	0.005	27	0.005	87	0.004	66	0.001	20	0.003	22

<sup>a</sup> Z: Values are the median of at least 8 randomly chosen soil samples of the entire 30 samples taken 0.5 m along a transect.

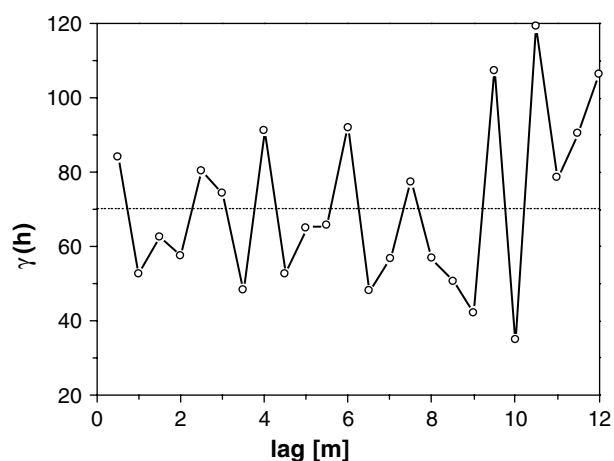
<sup>b</sup> CV, coefficient of variation (%).



**Figure 4.** Distribution of the measured atrazine concentrations in the soil profile on 09 May, 02 and 06 June in three depths: ( $\Delta$ ) 0–0.02 m, ( $\bullet$ ) 0.02–0.04 m, ( $\circ$ ) 0.04–0.06 m.

rates.<sup>4,22,26,46–48</sup> However, the study described in this paper focuses on horizontal spatial variability.

Chammas *et al.*<sup>27</sup> found both a high lateral and vertical variability for atrazine in their small-scale study. The variability for atrazine was much higher (CV 26–353%) than that for the conservative tracer chloride. The authors concluded that the variability was due to preferential atrazine transport and also to the variability in sorption properties of the soil. Other studies<sup>20,22</sup> showed that on larger scales herbicide residues are significantly correlated with



**Figure 5.** Experimental semivariogram of the atrazine concentrations for May 03. The dotted line represents the variance of the concentrations.

parameters controlling sorption, such as soil pH and organic carbon content. Less than 20% of the total semivariance in atrazine sorption coefficients was found at lag distances <10 m in a field trial (6.25 ha) conducted by Novak *et al.*<sup>8</sup> Little sorption variability was detected at the small scale, but atrazine sorption was influenced by landscape position and soil series on larger scales. Similarly, in a field experiment on two scales (0.1 ha and 1 m<sup>2</sup>) Beck *et al.*<sup>49</sup> showed that the variation of isoproturon sorption coefficients was less at the local scale than at the field scale. Lafrance and Banton<sup>50</sup> showed through a stochastic approach that the variability of soil parameters controlling water flow could be greater than that of the sorption-related parameters. Previous research and modelling indicate that the variability in sorption rates is less important for the small-scale horizontal variability of herbicide residues.

The observed horizontal variability might also be caused by uneven atrazine degradation in the field. This assumption is supported by the work of Walker *et al.*<sup>51</sup> who reported non-uniform herbicide degradation within a field (5 ha), incubating 30 soil samples collected from the field, fortified with isoproturon in the laboratory. Half-lives (ie time for 50% degradation of the initial amount of a pesticide) ranged from 6.5 to 30 days. The variability was ascribed to differences in the microbiological population influenced by soil pH. Other authors emphasizing the spatial variability of degradation within a single field are Beck *et al.*<sup>49</sup> and Vischetti *et al.*<sup>23</sup>

Another non-uniform process that could have taken place is preferential flow, where the solutes are transported through only a small portion of the soil volume. The probability of sampling these pathways is very low even if multiple soil cores are analysed. Preferential flow mechanisms therefore, in addition to enhancing pesticide mobility, may lead to horizontal variability and also to higher than expected pesticide mobility.<sup>11,27,52,53</sup>

### 3.3 Correlation between soil water content and atrazine concentrations

There was a significant positive correlation ( $P < 0.01$ ) between the two parameters for the samples collected directly after the application and for the samples collected one month after herbicide application (Table 5). For all other samples atrazine concentrations were not significantly correlated with soil water content. Several studies have indicated that the initial soil water content influences leaching of pesticides<sup>54</sup> by affecting the flow of infiltrating water which, in turn, affects leaching of a pesticide applied to the soil surface. Higher atrazine concentrations were found in areas of high soil water content in the first month of the experiment.

### 3.4 Dissipation of atrazine in the field experiment

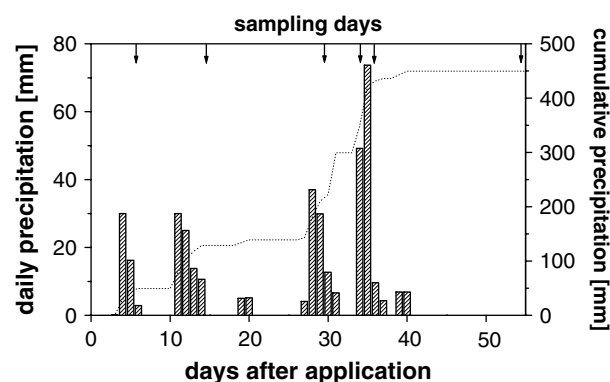
The average soil temperature was 7.5 °C and ambient temperature averaged 15 °C during the investigation period. The rainfall distribution during the 55-day experimental period following pesticide application on 3 May 2000 is shown in Fig 6. The total rainfall amounted to 410 mm. Soil samples were taken on May 9, May 15, June 2, June 6, June 8 and June 26 according to the rainfall distribution.

Background levels of atrazine were negligible, at  $0.66 \mu\text{g kg}^{-1}$  soil in the 0.08–0.16 m depth samples.

**Table 5.** Coefficient of correlation ( $r_s$ ) between soil water content and atrazine concentration in the soil measured at the six sampling days

Sampling date	Sampling depth (m)	Coefficient of correlation <sup>a</sup>
03.05.00	0–0.02	0.405**
09.05.00	0–0.02	0.206
	0.02–0.04	0.161
	0.04–0.06	0.136
15.05.00	0–0.02	0.095
	0.02–0.04	0.236
	0.04–0.06	0.475**
	0.06–0.08	0.305
	0.08–0.1	0.345
	0.1–0.12	0.642
	0.12–0.14	0.714
02.06.00	0–0.02	0.761**
	0.02–0.04	0.600**
	0.04–0.06	0.686**
06.06.00	0–0.02	0.581**
	0.02–0.04	0.483**
	0.04–0.06	0.445**
	0.06–0.08	0.400
26.06.00	0–0.02	0.233
	0.02–0.04	0.293
	0.04–0.06	0.679
	0.06–0.08	0.738**
	0.08–0.1	0.341
	0.1–0.12	0.533*
	0.12–0.14	0.001

<sup>a</sup> \* $P < 0.05$ , \*\* $P < 0.01$ .

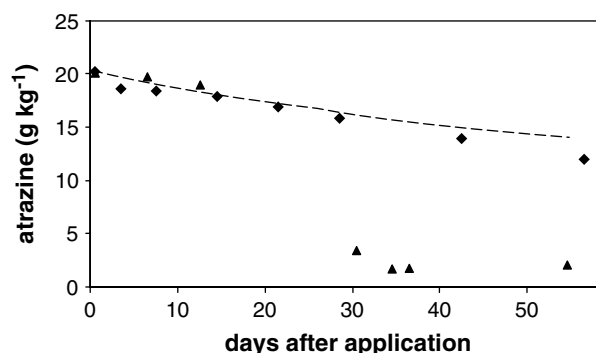


**Figure 6.** Daily precipitation, cumulative precipitation and sampling days (marked with arrows) during the investigation period from 03 May to 26 June, 2000.

In the other depths (0–0.08 m and 0.16–0.20 m) no atrazine could be detected. On average we recovered 102% of the amount applied in the top 2 cm of the soil profile 2 h after application.

The amount of atrazine in the profile was calculated from the measured concentrations and the bulk density for each depth increment, and then summed to obtain the total for the soil. The results from the second sampling (6 days after application) were inconsistent as the average concentrations and resulting amounts were about 5% higher than those on the day of the atrazine application. Therefore, these data were excluded from the discussion of the individual results but were included in the graphics and calculations.

Dissipation showed three phases (Fig 7). Within the first 12 days dissipation was slow. The average mass of atrazine found 12 days after application showed a reduction of 30% in the topsoil layer (0–0.02 m), after 118 mm of rainfall during the elapsed time period (Table 3). During the following 18 days dissipation was very fast: the average concentration in the first soil layer declined sharply to reach only about 10% of the original concentration; the further rainfall amounted to 111 mm, which had occurred mainly in a single event on 30th of May to 1st of June (Fig 6). This time-period was the early stage of soil–herbicide interaction, where the labile pool atrazine fraction



**Figure 7.** Comparison of atrazine dissipation (▲) in the field, (◆) in the laboratory and (- - -) predicted values using the laboratory half-lives corrected for temperature changes applying the Arrhenius equation.

would be more abundant than the fixed fraction. Afterwards dissipation slowed markedly. The pesticide was probably already more tightly bound in the soil and thus less prone to degradation and leaching, including any preferential flow.

Dissipation of atrazine can reasonably be described by a first-order exponential decay ( $r^2 = 0.85$ ) using the average mass data (Table 2). The resulting dissipation half-life of 12 days is significantly shorter than the degradation half-life of 79 days derived from our laboratory degradation study at 10 °C. To allow extrapolation of laboratory half-lives to the varying temperature conditions in the field, the Arrhenius equation was applied:

$$k = k_{\text{ref}} \exp \left[ - \left( \frac{E_A}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (3)$$

in which  $k$  is the rate coefficient ( $\ln(2)/DT_{50}$ ),  $k_{\text{ref}}$  is the rate coefficient at the reference temperature  $T_{\text{ref}}$ ,  $E_A$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K).<sup>55</sup> The mass balance could not be improved by correcting laboratory degradation rate by temperature (Fig 7). Loss of atrazine in the laboratory corrected by the actual field temperature only accounted for 35% of the field dissipation.

Field half-lives determined for samples from the different sampling depths were even shorter: 9 and 12 days for the depths of 0–0.02 m and 0.02–0.04 m, respectively. First-order decay functions fit the dissipation for these two soil layers, suggesting that degradation was the dominating process involved. Our observations indicate that the mass of atrazine stayed near the soil surface and degraded faster than in the laboratory study. In deeper soil layers (0.04–0.2 m) different processes gained importance, and dissipation could not be fitted by a first-order decay function. This suggests that additional loss processes were operating. The measured dissipation was significantly faster than in many previous field studies, in which half-life values for atrazine based on soil core recovery values ranged from 40 to 215 days.<sup>43,46,56–58</sup> Ghidry *et al.*<sup>20</sup> reported a half-life of 12 days for atrazine in a field trial (35 ha) on claypan soils. Gish *et al.*<sup>42</sup> calculated a similar unexpected short persistence time for atrazine during a 30-day field study with 318 mm of rain after applying atrazine to a fallow silt loam soil and explained it by preferential flow mechanisms. The study by Guo and Wagenet<sup>59</sup> gives another possible explanation for the difference between laboratory and field half-lives: they compared laboratory dissipation data derived from incubation experiments and column leaching experiments. Degradation rate coefficients measured in the column experiment were at least twice as fast as those measured in the incubation experiment, indicating that non-equilibrium transport favoured the herbicide degradation.

Atrazine was detected in the second and third soil layer (0.02–0.04 m and 0.04–0.06 m) at very

low concentrations ten days after application. At this stage randomly chosen samples from deeper soil layers (0.06–0.3 m) contained no residues of atrazine. Twelve days after its application, atrazine was detected at depths below 0.06 to 0.16 m, but only in very low concentrations. During the total period of investigation no significant concentrations of atrazine was detected in the experimental depth of 0.06–0.3 m (Table 4). This indicates that in the loamy high organic matter soil atrazine could not reach deeper layers within 55 days through matrix flow.

Throughout the investigation period the atrazine distribution within the profile showed a maximum concentration in the top 0.02 m of the soil with concentrations declining to 0.3 m depth (Tables 3 and 4). For the last sampling date, 55 days after application, the depth for maximum concentration was 0.01 m. The centre of the mass distribution was at 0.021 m. This discrepancy between centre of the mass and maximum concentration is also evidence of non-equilibrium in the dissipation process.

Together these observations suggest that atrazine was degraded faster than in the laboratory. First, the high CVs of the atrazine concentrations and the lack of a spatial structure indicate that non-uniform processes took place. Second, first-order decay functions reasonably fit the atrazine dissipation suggesting that degradation was a dominating process. The high sorptive capacity of this soil and the lack of strong structure or preferential paths make the alternative hypothesis of rapid leaching of large quantities of atrazine to below 0.3 m unlikely. Even though, in loamy soils, there is evidence that pesticides can move along preferential pathways,<sup>46,52,60</sup> in our study the lack of evidence of any atrazine below the surface area would suggest that unexpected fast degradation took place. Unfortunately, no further field data (soil samples from deeper depths) are available to evaluate the two potential explanations.

#### 4 CONCLUSIONS

- (1) Our results question the assumption that degradation in the field under dynamic flow conditions and under changeable temperature and soil water content conditions can be characterized by laboratory half-lives determined under controlled static conditions. We conclude that degradation in the field is a spatially variable process and transport-dependent. This should be considered in modelling the dissipation of pesticides.
- (2) The results described here may be used for improving the sampling methodology for pesticide residue studies. The observed CVs for pesticide concentrations were quite high and significantly higher than those of soil water content. This emphasises the need to analyse multiple soil cores for making assumptions on pesticide persistence in soils.

- (3) The study raises warning flags for future experimental efforts of this type. No valid spatial structure at this scale for the pesticide concentrations could be inferred. Either the measurement resolution was still too coarse, as the ranges of the respective semivariogram models would be smaller than 0.5 m, or the horizontal variabilities of soil pesticide concentrations are of a stochastic nature. The spatial resolution of measurements should generally be much higher to derive potential short-range correlation structures. If processes like preferential flow govern the pesticide dissipation, the small-scale geostatistics of soil properties would be required. Spatial distribution of variables can be a basis for future stochastic simulations of the mass transfer in soil including preferential flow.
- (4) The high horizontal variability of pesticide concentrations, the biphasic decay in the subsoil and the unexpected fast dissipation suggest the presence of non-uniform processes. Experimental mass recoveries for atrazine in June were small. Mass balances are a crucial point even in a field experiment with a high sampling resolution, such as this study. In future investigations a dye tracer could be used to visualize actual flow paths,<sup>61</sup> to assist in deciding the depth to which samples should be collected for pesticide study, and to verify if preferential flow is likely to occur on the site.

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